Mössbauer spectroscopic study of some iron and antimony – containing minerals

Mössbauer spectroscopic study of some iron and antimony – containing minerals

2010 J. Phys.: Conf. Ser. 217 012049

(http://iopscience.iop.org/1742-6596/217/1/012049)

Journal of Physics: Conference Series **217** (2010) 012049 doi:10.1088/1742-6596/217/1/012049

Mössbauer spectroscopic study of some iron and antimony – containing minerals

R Bayliss[1], F J Berry[1,2,4], A Bowden[2], C Greaves[1] and M F Thomas[3]

[1] School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

[2] Department of Chemistry, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom

[3]Department of Physics, The University of Liverpool, Liverpool L69 3BX

[4]To whom any correspondence should be addressed : f.j.berry@open.ac.uk

Abstract Iron-57 Mössbauer spectra have been recorded from three minerals containing both iron and antimony. Schafarzikite of composition $FeSb_2O_4$ contains Fe^{2+}. The ^{121}Sb Mössbauer spectrum shows only the presence of Sb^{3+}. The ^{57}Fe Mössbauer spectrum corresponds with that recorded from a material of identical composition synthesised by a solid state reaction during the course of this work. Apuanite of formulation $Fe_{20}Sb_{16}O_{48}S_4$ contains both Fe^{2+} and Fe^{3+} in the ratio 1:3.35 The result is consistent with crystal structure determinations and the formulation of apuanite as $Fe_4^{2+}Fe_{16}^{3+}Sb_{16}O_{48}S_4$. Versiliaite of composition $Fe_{12}Sb_{12}O_{32}S_2$ contains $Fe^{2+}$and Fe^{3+} in the ratio 1:2.12 and, also consistent with structural characterisations, can be formulated $Fe_4^{2+}Fe_8^{3+}Sb_{12}^{3+}O_{32}S_2$.

1. Introduction

The application of Mössbauer spectroscopy for the characterisation of minerals has been known for many years [1]. We are beginning a programme of synthesis and characterisation of inorganic solids containing iron and antimony and have become aware of minerals containing these elements which appear to have received sparse attention in the past. As a preliminary to the main body of work we have examined, for the first time, the ^{57}Fe Mössbauer spectra from three minerals containing iron and antimony.

Schafarzikite was first identified in the Slovak Republic in 1921 [2] and was subsequently shown to adopt the composition $FeSb_2O_4$[3]. The mineral has been characterised by X-ray diffraction and described [4] in terms of columns of edge–sharing iron-containing octahedra connected by corner sharing to parallel chains of three-coordinate pyramidal antimony. The mineral is rare but after no findings for over eighty years has recently been found near Pernek also in the Slovak Republic [5]. Schafarzikite is the parent phase of apuanite, $Fe_{20}Sb_{16}O_{48}S_4$, and versiliate, $Fe_{12}Sb_{12}O_{32}S_2$, found in the Apuan Alps in Italy. Apuanite and versiliaite are derived from schafarzikite by substitution on some antimony sites by iron [6,7] and the insertion of sulphide bridges between these iron ions. We report

here on the characteristion of the iron oxidation states in schafarzikite and a synthetic analogue made during the course of this work and in apuanite and versiliaite by Mössbauer spectroscopy.

2. Experimental

Schafarzikite from the Kriznica mine, Pernek, Slovak Republic [5] was obtained from Systematic Mineralogy, Czech Republic. Apuanite and versiliaite from the Bucca della Vena Mine, Alpuan Alps, Italy [6,7] were obtained from Roger's Minerals, Canada. A sample of $FeSb_2O_4$ was prepared by heating a stoichiometric mixture of α– iron(III) oxide and antimony(III) oxide in air at 925^0C for 24 hours to produce iron antimonate ($FeSbO_4$). The iron antimonate was heated with an appropriate amount of elemental antimony in an evacuated sealed silica tube at 600^0C for 24 hours. The product was ground and heated again in an evacuated sealed silica tube at 600^0C for 24 hours to give single phase $FeSb_2O_4$.

Mössbauer spectra were recorded at 298K (^{57}Fe) and 77K (^{121}Sb) with a constant acceleration spectrometer in transmission geometry using a 400 MBq ^{57}Co/Rh and a 0.6 mCi $Ca^{121m}SnO_3$ source. The drive velocity was calibrated with the ^{57}Co/Rh source and a natural iron foil. All the chemical isomer shift data are reported relative to that of metallic iron at 298K.

3. Results and discussion

3.1 Schafarzikite

The ^{57}Fe Mössbauer spectra recorded from schafarzikite, apuanite, versiliate and the synthesised $FeSb_2O_4$ are shown in Figures 1-3. The ^{57}Fe Mössbauer parameters are collected in Table 1.

The ^{57}Fe Mössbauer spectrum recorded here from the recently discovered sample of schafarzikite [5] (Figure 1a) was dominated by a quadrupole split absorption characteristic of Fe^{2+}. The ^{121}Sb Mössbauer spectrum showed a resonance, δ= -11.84 mms^{-1}, charactaristic of Sb^{3+}. The result is consistent with the structural description of earlier–[4] and recently–[5] found samples of schafarzikite from which chains of FeO_6 octahedra, held together by chains of 3-coordinate antimony in which the lone pairs of electrons on Sb^{3+} point into the channels, can be envisaged. A doublet corresponding to Fe^{3+} was observed in the spectrum but, given that schafarzkite is found with other iron-containing minerals [2,5] ,we associate this with a minority impurity phase. Indeed X-ray powder diffraction showed weak reflections not attributable to schafarzikite but which could not be unequivocally associated with another Fe^{3+}-bearing mineral.

The spectrum recorded from the synthesised material of composition $FeSb_2O_4$ (Figure 1b) showed a single quadrupole split absorption with a chemical isomer shift characteristic of Fe^{2+}.

3.2 Apuanite

The ^{57}Fe Mössbauer spectrum is shown in Figure 2. The spectrum was best fitted to two components characteristic of Fe^{2+} and Fe^{3+}. The peak area ratio of the Fe^{2+} to Fe^{3+} components was *ca*. 1: 3.35 (Table 1). The result validates the structural description [6,7] in terms of the substitution of every third antimony cation in the pyramidal chains of schafarzikite by an Fe^{3+} ion with pairs of these ions being linked by the sulphide anions; charge balance is achieved by oxidation of some Fe^{2+} within the chains. The results recorded here are consistent with the formulation of apuanite as $Fe_4^{2+}Fe_{16}^{3+}Sb_{16}^{3+}O_{48}S_4$

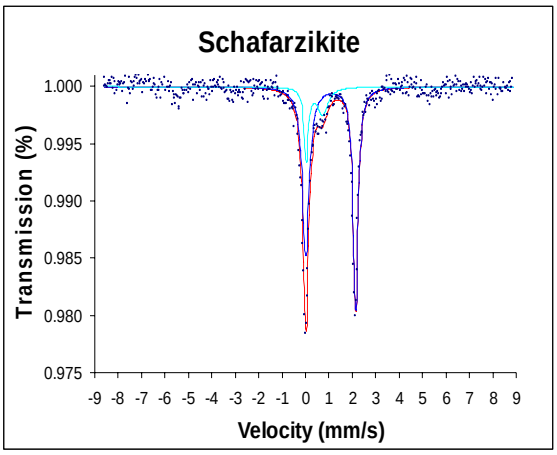

Figure 1a. ^{57}Fe Mössbauer spectrum recorded from schafarzikite

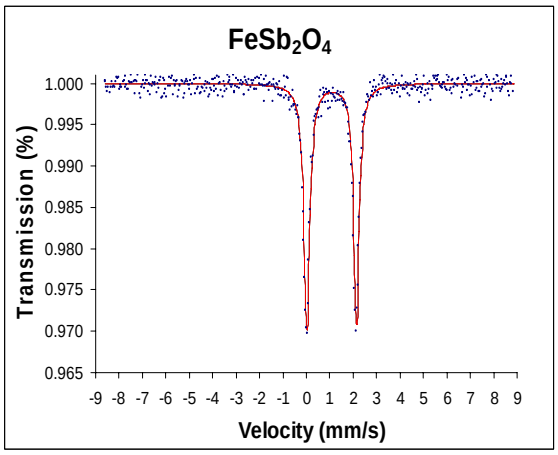

Figure 1b. ^{57}Fe Mössbauer spectrum recorded from $FeSb_2O_4$

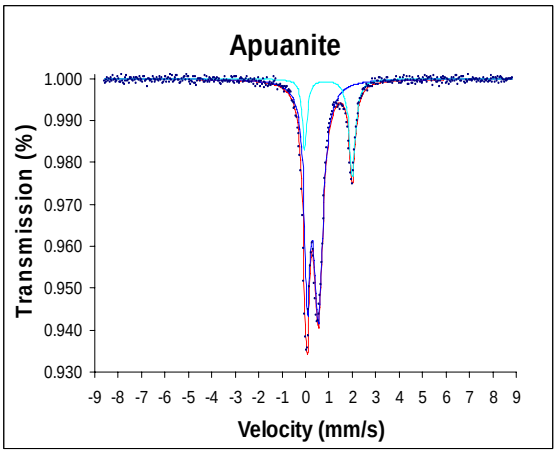

Figure 2. ^{57}Fe Mössbauer spectrum recorded from apuanite

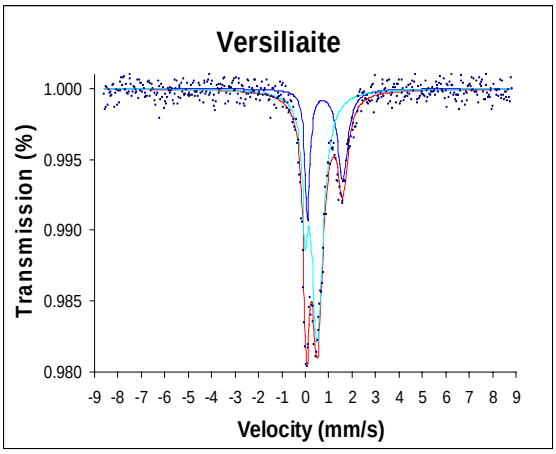

Figure 3. ^{57}Fe Mössbauer spectrum recorded from versiliaite

3.3 Versiliaite

The ^{57}Fe Mössbauer spectrum is shown in Figure 3. The spectrum was again fitted to two components characteristic of Fe^{2+} and Fe^{3+} but with a peak area ratio of 1:2.12 (Table 1). This result is also consistent with the structural description of versiliate [6, 7] involving the substitution of every fourth Sb^{3+} cation in the pyramidal chains of schafarzikite by an iron ion and the insertion of sulphide anions with corresponding oxidation of Fe^{2+}. The results recorded here are consistent with the formulation of versiliaite as $Fe_4^{2+}Fe_8^{3+}Sb_{12}^{3+}O_{32}S_2$.

Table 1. ^{57}Fe Mössbauer parameters recorded at 298K from schafarzikite-related structures.

Sample		$\delta \pm 0.02$/mms^{-1}	$\Delta \pm 0.02$/mms^{-1}	Area ± 2 %
Schafarzikite	Fe^{2+}	1.08	2.13	80
	Fe^{3+}	0.38	0.69	20
$FeSb_2O_4$	Fe^{2+}	1.08	2.11	100
Apuanite	Fe^{2+}	0.99	2.03	23
	Fe^{3+}	0.32	0.47	77
Versiliaite	Fe^{2+}	0.85	1.50	32
	Fe^{3+}	0.25	0.51	68

4. Conclusions

A material of composition $FeSb_2O_4$ containing only Fe^{2+} identical to that of the mineral schafarzikite has been prepared. ^{57}Fe Mössbauer spectroscopy shows the minerals apuanite and versiliaite to contain both Fe^{2+} and Fe^{3+} consistent with predictions from crystal structure determinations.

5. References

[1] Bancroft G M 1973 *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemisty* Maidenhead: McGraw-Hill
[2] Krenner J A 1921 *Z. Kristallogr*. **56** 198
[3] Zemann J 1951 *Tschermaks Mineral. Petrog. Mitt*. **2** 166
[4] Fischer R and Pertlik F 1975 *Tschermaks Mineral. Petrog.Mitt*. 22, 236
[5] Sejkora J, Ozdin D, Vitalos J, Tucek P, Cejka J and Duda R. 2007 *Eur. J. Mineral*. **19** 419
[6] Melini M, Merlino S and Orlandi P *Amer. Min.* **64** 1230
[7] Mellini M and Merlino S 1979 *Amer. Min.* **64** 1235